



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In reapplication of: Bowie G. Keefer et al.

Application No.: 09/591,277

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Confirmation No.: 3353

For: CHEMICAL REACTOR WITH PRESSURE
SWING ADSORPTION

Examiner: Wayne L. Langel

Art Unit: 1754

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CERTIFICATE OF MAILING

I hereby certify that this paper and the documents referred to as being attached or enclosed herewith are being deposited with the United States Postal Service as First Class Mail in an envelope addressed to: MAIL STOP ISSUE FEE, COMMISSIONER FOR PATENTS, P.O. BOX 1450, ALEXANDRIA, VA 22313-1450 on the date shown below.

Attorney or Agent
for Applicant(s) Wayne L. Langel

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**REMINDER CONCERNING FOREIGN PRIORITY CLAIM
UNDER 35 U.S.C. § 119**

A review of the file record in the U.S. Patent and Trademark Office's (USPTO) PAIR database and the Filing Receipt reveals that the USPTO apparently has not made of record the foreign priority claim made in connection with the present application.

The executed Declaration filed with the present application identified and claimed priority under 35 U.S.C. § 119 to the following priority applications:

- (1) Canadian Application No. 2,274,300 filed June 10, 1999; and
- (2) Canadian Application No. 2,274,301 filed June 10, 1999

The application transmittal letter also claimed priority to these two Canadian applications. Certified copies of the Canadian applications are submitted with payment of the issue fee.

Accordingly, applicants respectfully request that the USPTO make of record (and the issued patent reflect) the properly made claim for foreign priority.

Respectfully submitted,

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This is to certify that the documents attached hereto and identified below are true copies of the documents on file in the Patent Office.

Specification and Drawing, as originally filed, with Application for Patent Serial No: CA 2274300, on June 10, 1999, by QUESTOR INDUSTRIES INC., assignee of Bowie G. Keefer and Denis J. Connor, for "Chemical Reactor System".

Agént certificateur/Certifying Office

Agent certificate, certifying Office

September 13, 2006

Date

Canadä

(CIPO 68)
31-03-04

OPIC CIPO

Chemical Reactor System

Inventors: Bowie G. Keefer and Denis J. Connor

Important applications exist where the separation of carbon dioxide is desired at elevated temperature from a gas mixture containing steam, or where such separation could greatly enhance process efficiency, simplicity and economics.

The important process of steam reforming is used to generate hydrogen rich gas from methane and other light hydrocarbons, for example to produce hydrogen or ammonia. This highly endothermic reaction is conducted at 800° to 1000° C degrees over typically a nickel catalyst which must be reduced. High temperature is required to achieve satisfactory conversion, with the penalty that at such high temperature the water gas shift equilibrium is unfavourable so that approximately half the carbon goes to carbon monoxide. Heat supply to the reaction is a technical challenge and an economic burden. Subsequent to steam reforming, the moderately exothermic water gas shift reaction must be conducted at lower temperature (e.g. 250° to 400° C) to react the carbon monoxide with steam to generate carbon dioxide plus hydrogen. Even then, the conversion of carbon monoxide is incomplete so that further purification is required, while the energy value of that carbon monoxide is lost. Carbon monoxide is a poison to many uses of hydrogen, including powering low temperature fuel cells, ammonia synthesis and petroleum refining.

If carbon dioxide could be separated at temperatures between 600° and 800° C, the steam reforming reaction could be conducted under much more favourable conditions. Abstraction of carbon dioxide from the reacting gas stream would drive the reaction forward to consume methane (at lower temperature if desired), while forcing the water gas shift reaction to consume carbon monoxide. The directly produced final product is then hydrogen, substantially purified apart from any inert components and residual steam; while the endothermic heat requirement of hydrogen production is significantly lowered by the cancellation of the water gas shift heat of reaction.

The reaction of lime as a "carbon dioxide sorbent" to calcium carbonate has long been recognized as a basic technique for removal of carbon dioxide from syngas mixtures produced by steam reforming, or by partial oxidation of heavier hydrocarbons or gasification of coal or biomass. The reaction of calcium oxide and calcium carbonate is very exothermic, approximately balancing the endothermic heat demand of the steam reforming reaction producing that amount of carbon dioxide. Hence, contacting lime with the reacting gas stream is a way to meet its heat demand as well as to remove the CO₂. Extensive work has been done in development of "carbon dioxide sorbent" processes using fluid bed reactors, with the lime (typically in a mixed compound with dolomite for durability) circulating as CO₂ sorbent particles which may be separated by size and density from the circulating catalyst pellets. The loaded CO₂ sorbent is then thermally regenerated to release the CO₂, in a regeneration furnace separate from the steam reforming

reaction zone. Typically, the regeneration step is directly fired by the admission of air or oxygen to react with some of the fuel gas.

Unfortunately, reversing the calcium oxide / calcium carbonate reaction is destructive on typical pellet compositions, resulting in pore blockage, structural breakdown and attrition so that the CO₂ sorbent has had only a limited life in terms of numbers of cycles. A very interesting announcement has been made by Air Products and Chemicals, of an improved sorbent with much higher durability than the earlier art.

Lyon has disclosed a so-called "Unmixed Reforming" reformer to generate hydrogen for fuel cells, using a CO₂ sorbent in a fixed bed format, with the steam reforming catalyst intimately mixed in the same fixed bed. This concept requires that the nickel catalyst be cycled from reduced to oxidized states in each regeneration cycle, which may be expected to reduce the catalyst surface area and effective activity.

The present invention contemplates that the CO₂ sorbent (e.g. CaO as a chemically active sorbent), or other CO₂ sorbent functional at elevated pressure and temperature in the presence of steam, be supported as a "sorbent laminate" in a composite matrix formed as thin sorbent sheets and laminated with spacers to define parallel flow channels between the sorbent sheets. The inventor has found such laminated sheets, reinforced with glass fibers, wire mesh or a metal foil, and impregnated with zeolite crystallites, to be highly effective in gas separation at more ordinary temperatures. For high reaction temperatures with the CO₂ sorbent, the reinforcement matrix of the sorbent sheets would desirably be provided by refractory ceramic fibers, with a mesoporous or macroporous binder matrix to immobilize the sorbent as finely divided particles of ultrathin coatings. Suitable binders may include clays, hydrophobic zeolites, and mesoporous forms of silica. Metallic fibers and binders may also be contemplated. Substitute or complement carbonate-forming metals for calcium include magnesium, cadmium, iron, copper, and zinc. By suitable compounding, the working temperature for sorption and desorption may be optimized. Physical integrity may be enhanced by an admixture of barium or strontium carbonates, themselves unreactive under process conditions. The sorbent laminate configuration reduces resistances of mass transfer, heat transfer and pressure drop, while retaining the CO₂ sorbent in a durable structure for extended cycling at much higher frequency than previously contemplated.

The inventor has previously investigated use of hydrophobic high silica zeolites, e.g. silicalite, as CO₂ sorbents which would rely on physical rather than chemical sorption. Dealuminified Y zeolite, chabazite or mordenite could also be used as CO₂ sorbents capable of operation in the presence of water vapour. Such adsorbents may also be exchanged with copper or other transition elements to enhance CO uptake and water gas shift reactivity.

The present invention contemplates that regeneration of the CO₂ sorbent (in the preferred form of fixed beds of sorbent laminate) will be achieved by pressure swing, thermal swing or preferably a combination thereof; with the flow through each sorbent laminate bed alternatingly in a first "feed" direction for sorbing CO₂ and rejecting heat (e.g. to a steam reforming reaction) and then in the reverse "exhaust" direction for desorbing CO₂ while accepting heat. The invention provides that the source and direction of flow through the sorbent laminate beds shall be controlled by multiport rotary valves communicating to the ends of each sorbent bed. Most preferably, the sorbent beds are mounted at equally spaced angular stations on a rotary wheel, whose face(s) engaging its enclosing stator housing will provide the multiport valving function with a single moving part. The inventor has disclosed an analogous device for pressure swing adsorption using zeolite adsorbent laminates.

With respect to the rotary axis of the wheel, the flow path through the sorbent beds may be radial or axial at each valving face, so that the valve face would be respectively a circular cylinder or a flat disc.

If the sorbent laminate matrix has been formed with a metal fiber or binder which is catalytically active for steam reforming, or a catalyst component is provided as a separate additive in the laminate or its spacers, the steam reforming reaction may be conducted within the flow channels of the sorbent laminate in the wheel. Regeneration must then be achieved with heat provided to the flow of the exhaust direction, either directly by combustion of fuel gas (feedstock or hydrogen mixture) with air or oxygen, or indirectly by heat transfer. Oxidation of the catalyst may be avoided if it sufficiently incorporates a noble metal such as platinum or palladium. Otherwise, the catalytic surface will undergo cyclic oxidation/reduction, as in the invention of Lyon.

Cyclic oxidation/reduction of the catalyst may be avoided by placing the catalyst in the housing at a feed port. To obtain high conversion, the process may be multistaged as follows, within a rotary wheel apparatus with the functional schematic as shown in Fig. 1. Sorbent beds 1 to 11 are mounted in a wheel that rotates them sequentially past the positions shown, as indicated by arrows 12 and 13. The feed direction in each bed is downward, and the exhaust direction is upward. Feed (e.g. natural gas with steam) is admitted from preheater 20 through first stage catalyst bed 21 to sorbent bed 1 which takes up CO₂ generated in the catalyst bed 21. The effluent from sorbent bed 1 is then conveyed by cross-over duct 22 to second stage catalyst bed 23 with associated heat exchangers to maintain a desirable thermal profile. Similarly, further catalyst bed stages carry the reaction further to completion, feeding successive sorbent beds whose initial CO₂ loading is lower to achieve higher hydrogen concentration. The final stage feeds sorbent bed 5 which is initially most depleted in CO₂, and which delivers hydrogen product of purity dependent on the number of stages from product delivery conduit 25.

Preferably although not necessarily, thermal regeneration of the sorbent beds is assisted by a pressure swing, under which beds 1 - 5 operate at a higher working

pressure for feed, and beds 7 – 10 operate at a lower working pressure for exhaust. Sorbent bed 11 (which was in the position of bed 1 in the previous step of the cycle) is undergoing pressure release through valve or expander 30, venting some natural gas and CO₂ into bed 10 or others of beds 7- 10. Bed 6 (which was in the position of bed 7 in the previous step of the cycle) is being repressurized with product hydrogen by a valve or expander 32, while bed 7 is being purged by product hydrogen (after pressure let-down by valve 33) and/or by a mixture of fuel gas and air. In each of beds 7 – 10, thermal regeneration may be achieved by direct combustion of fuel gas and/or hydrogen with appropriately injected oxygen or air as suggested by dashed arrows 35, or else by indirect heating through heat exchangers 40 in the cross-over ducts 41 linking sequentially each pair of beds in the regeneration stages occupied by sorbent beds 7 – 10. The regeneration gas containing CO₂ desorbed from the beds undergoing regeneration is thus conveyed through the beds as shown with successive reheating, and finally discharged as rich CO₂ from the exhaust 50 of bed 10. It will be apparent that the number of reaction stages (1 – 5) and regeneration stages (7 – 10) may be selected to achieve optimal productivity and hydrogen purity.

FIG. 1

